

The Pinacol-Pinacolone Rearrangement

1. The Rearrangement of Pinacols Containing the Biphenylene Group
2. The Rearrangement of Unsymmetrical Aromatic Pinacols

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Helen Ruth Sternberger
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ACKNOWLEDGMENT

The author welcomes this opportunity to express her grateful appreciation to Professor W. E. Bachmann who suggested this problem and whose patient guidance and encouragement has made possible its completion.

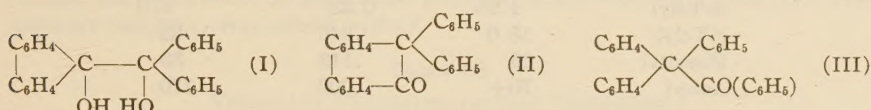


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The Pinacol-Pinacolone Rearrangement. IV. The Rearrangement of Pinacols Containing the Biphenylene Group

BY W. E. BACHMANN AND HELEN R. STERNBERGER¹

Meerwein² found that diphenylbiphenyleneglycol (I) on treatment with sulfuric acid gives 10,10-diphenylphenanthrone (II) but does not give any of the isomeric benzoylphenylfluorene (III) by migration of the phenyl



group. Recently, Bergmann and Schuchardt³ observed that dehydration by acetyl chloride gives benzoylphenylfluorene (III) and no diphenylphenanthrone. Furthermore, their discovery that benzoylphenylfluorene is isomerized into diphenylphenanthrone by sulfuric acid makes it appear probable that benzoylphenylfluorene is the true product of the rearrangement.

We find that diphenylbiphenyleneglycol (I) when treated with acetyl chloride actually gives a mixture of diphenylphenanthrone and benzoylphenylfluorene and not a single product as has been reported. Similarly,

TABLE I
REARRANGEMENT OF PINACOLS

Group Ar	Products	%	Group migrated
Phenyl	Benzoylphenylfluorene	78	Phenyl
	Diphenylphenanthrone	22	Biphenylene
<i>m</i> -Tolyl	<i>m</i> -Toluyyl- <i>m</i> -tolylfluorene	54	<i>m</i> -Tolyl
	Di- <i>m</i> -tolylphenanthrone	46	Biphenylene
<i>p</i> -Tolyl ⁴	<i>p</i> -Toluyyl- <i>p</i> -tolylfluorene	14	<i>p</i> -Tolyl
	Di- <i>p</i> -tolylphenanthrone	86	Biphenylene
Anisyl ⁴	Anisoylanisylfluorene	2	Anisyl
	Dianisylphenanthrone	98	Biphenylene
Phenetyl	<i>p</i> -Ethoxybenzoylphenetylfluorene	4	Phenetyl
	Diphenetylphenanthrone	96	Biphenylene

(1) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(2) Meerwein, *Ann.*, **396**, 200 (1913).

(3) Bergmann and Schuchardt, *ibid.*, **487**, 225 (1931).

(4) Bergmann and Schuchardt obtained a single rearrangement product.

two rearrangement products, corresponding to (II) and (III), are obtained from four other pinacols. The results are presented in Table I.

Giving a value of unity to the migration aptitude of the phenyl group one has the following series representing the relative migration aptitudes of the groups in biphenylene pinacols: phenyl, 1.0; *m*-tolyl, 0.33; biphenylene, 0.31; *p*-tolyl, 0.046; phenetyl, 0.012; anisyl, 0.006. The migration aptitudes of five of these groups, phenyl, *m*-tolyl, *p*-tolyl, phenetyl and anisyl, have been determined when they are situated in symmetrical pinacols.⁵ In Table II is given a comparison of the relative migration aptitudes of these five groups in the two types of pinacols.

TABLE II
MIGRATION APTITUDES

Group	M_s (symmetrical pinacol)	M_b (biphenylene pinacol)	$1/M_b$
Phenyl	1.0	1.0	1.0
<i>m</i> -Tolyl	1.95	0.33	3.0
<i>p</i> -Tolyl	15.0	.046	22
Phenetyl	66	.112	83
Anisyl	70+	.006	170

It is observed that the order in the two series is exactly reversed; moreover, the reciprocals of the values for the migration aptitudes in the biphenylene pinacols are roughly of the same order as the values for the symmetrical pinacols. We are preparing and rearranging a large number of pinacols in order to determine whether the relation holds true for the whole class of biphenylene pinacols.

Experimental

Preparation of the Pinacols.—The pinacols were prepared by the action of a Grignard reagent on the methyl ester of biphenyleneglycolic acid.^{2,3} A solution of 15 g. of the methyl ester was added to the Grignard reagent which had been prepared from 0.25 gram mole of aryl halide (*m*-bromotoluene, *p*-bromophenetole, etc.). After being refluxed for twelve hours the mixture was hydrolyzed. In this manner, dianisylbiphenyleneglycol, prepared by Bergmann and Schuchardt in 37% yield, was obtained by us in 80% yield. The yields and properties of the two new pinacols, di-*m*-tolylbiphenyleneglycol and diphenetyl biphenyleneglycol, are given in Table III.

Rearrangement of the Pinacols.—The pinacols were rearranged by a twenty-four hour treatment with acetyl chloride in benzene and acetic acid.⁵ This agent does not isomerize benzoylphenylfluorene.

Analysis of Pinacolone Mixtures.—The mixture of benzoylphenylfluorene and diphenylphenanthrone from 3.64 g. (0.01 mole) of diphenylbiphenyleneglycol was heated with a solution of 6 g. of potassium hydroxide in 100 cc. of absolute alcohol for six hours. This process cleaved the benzoylphenylfluorene into benzoic acid and phenylfluorene but left the diphenylphenanthrone unchanged. Five separate runs gave an average of 0.0070 gram mole of benzoic acid. This represents a 78% migration of the phenyl group since a 95% yield of total products was obtained and a 95% yield of benzoic acid resulted by scission of pure benzoylphenylfluorene.

(5) Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932), and unpublished results.

Practically the same results were obtained when both the benzoylphenylfluorene and the diphenylphenanthrone were cleaved, the latter being converted to 2-benzhydryl-2'-carboxylbiphenyl. The mixture of pinacolones was heated with a solution of 25 g. of potassium hydroxide in 100 cc. of methanol for three days. After removal of the solvent the product was treated with a mixture of water and benzene; potassium benzoate dissolved in the water while the potassium salt of the 2-benzhydryl-2'-carboxylbiphenyl was contained in the benzene layer along with phenylfluorene. Treatment with hydrochloric acid converted the salt to the free acid; when the mixture of phenylfluorene and acid was dissolved in hot *n*-propyl alcohol and the solution was allowed to cool, the phenylfluorene deposited first. The 2-benzhydryl-2'-carboxylbiphenyl was obtained in large colorless prisms; m. p. 175° with previous softening.⁶ The potassium salt of the acid is little soluble in dry benzene but dissolves readily in wet benzene or in wet ether; it can be obtained as colorless leaflets by recrystallization from methanol.

The mixtures of pinacolones obtained from the other pinacols were analyzed in a similar manner; the values given in Table I represent the averages of several runs which checked each other closely. Di-*p*-tolylphenanthrone and dianisylphenanthrone are cleaved into the biphenyl acids by six hours of heating with 6% potassium hydroxide in ethanol; the properties of the acids and of other compounds are given in Table III. The yields are based on recrystallized product.

TABLE III

YIELDS AND PROPERTIES OF NEW COMPOUNDS

Compound	Yield, %	M. p., °C.	Recryst. solvents	Cryst. form	Analyses, %	
					Calcd.	Found
Di- <i>m</i> -tolylbiphenyleneglycol	55	143.5-144.5	Acetone + alc.	Needles	C, 85.7 H, 6.2	85.2 6.2
Diphenetyl biphenyleneglycol	51	147-150	Acetone + alc.	Cubes	C, 79.6 H, 6.2	79.2 6.1
Di- <i>m</i> -tolylphenanthrone	62	198.0-198.5	Acetic acid	Diamond plates	C, 89.8 H, 5.9	89.6 6.0
Diphenetylphenanthrone	77	135.0-135.5	<i>n</i> -Propyl alc.	Fine needles	C, 82.9 H, 6.0	83.2 6.4
2-(Di- <i>p</i> -methylbenzhydryl)-2'-carboxybiphenyl ^a	76	193-194	<i>n</i> -Propyl alc.	Diamond plates	C, 85.7 H, 6.2	85.5 6.2
2-(Di- <i>p</i> -methoxybenzhydryl)-2'-carboxybiphenyl	75	136-137	<i>n</i> -Propyl alc.	Heavy needles	C, 79.2 H, 5.7	78.9 6.2

^a Bergmann and Schuchardt obtained an amorphous solid which they considered to be this acid from the reaction between ditolylphenanthrone and alkali.

Summary

Five pinacols containing the biphenylene group have been rearranged by acetyl chloride to mixtures of pinacolones. The order and extent of migration of the groups is the reverse of the migration aptitudes of the groups in symmetrical pinacols.

ANN ARBOR, MICHIGAN

RECEIVED MAY 27, 1933
PUBLISHED SEPTEMBER 5, 1933

(6) Compare Acree, *Am. Chem. J.*, **33**, 180 (1905).

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[Reprint from the Journal of the American Chemical Society, 56, 170 (1934).]

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The Pinacol-Pinacolone Rearrangement. V. The Rearrangement of Unsymmetrical Aromatic Pinacols

By W. E. BACHMANN AND HELEN R. STERNBERGER¹

Recently² an investigation of the rearrangement of unsymmetrical pinacols was begun; three pinacols of the type $RR(OH)CC(OH)R'R'$, in which R and R' are aryl groups, were subjected to rearrangement and the extent to which each of the two groups migrated was determined. We are now reporting the results obtained by rearrangement of seven new pinacols of this kind. In Table I are shown the percentage migration of the two groups in each pinacol; for comparison there is shown the migration of the same groups

when situated in the symmetrical pinacol $RR'-(OH)CC(OH)RR'$.

It is apparent that the groups migrate differently when situated in the two types of pinacols. In a number of cases the order of migration is reversed; that is, the group that migrates to the greatest extent in the symmetrical molecule migrates least when situated in the unsymmetrical pinacol. There is no simple relationship between the two sets of values.³ This is even more apparent from a comparison of the series

(1) Submitted in partial fulfillment of the requirements for the Ph.D. degree.

(2) Bachmann, *THIS JOURNAL*, **54**, 2112 (1932).

(3) For comparison with pinacols containing the biphenylene group see Bachmann and Sternberger, *ibid.*, **55**, 3819 (1933).

TABLE I
MIGRATION OF GROUPS

Groups R ₁ R'	Unsym. Migration,	Pinacol Sym., %
C ₆ H ₅	46	8
<i>p</i> -C ₆ H ₄ C ₆ H ₄	54	92
C ₆ H ₅	57	60
<i>p</i> -ClC ₆ H ₄	43	40
C ₆ H ₅	67	2.5
<i>p</i> -C ₂ H ₅ OC ₆ H ₄	33	97.5
C ₆ H ₅	91	35
<i>p</i> -FC ₆ H ₄	9	65
<i>p</i> -C ₆ H ₄ C ₆ H ₄	58	87
<i>m</i> -CH ₃ C ₆ H ₄	42	13
<i>p</i> -CH ₃ OC ₆ H ₄	45	96.7
<i>p</i> -CH ₃ C ₆ H ₄	55	3.3
<i>p</i> -CH ₃ OC ₆ H ₄	35	
<i>m</i> -CH ₃ C ₆ H ₄	65	
C ₆ H ₅ ²	72	1.4
<i>p</i> -CH ₃ OC ₆ H ₄	28	98.6
C ₆ H ₅ ²	51	6
<i>p</i> -CH ₃ C ₆ H ₄	49	94
C ₆ H ₅ ²	50	34
<i>m</i> -CH ₃ C ₆ H ₄	50	66

representing the relative migration aptitudes of the groups on the basis of phenyl as unity. For the unsymmetrical pinacols the following series holds: *p*-biphenyl, 1.18; phenyl, 1.0; *m*-tolyl, 1.0; *p*-tolyl, 0.96; *p*-chlorophenyl, 0.75; phenetyl, 0.49; anisyl, 0.39; *p*-fluorophenyl, 0.099. The corresponding series for the symmetrical pinacols is: anisyl, 70+, phenetyl, 39; *p*-tolyl, 15; *p*-biphenyl, 11.5; *m*-tolyl, 1.95; *p*-fluorophenyl, 1.85; phenyl, 1.0; *p*-chlorophenyl, 0.66. It is seen that there is much less variation in the series of migration aptitudes in the unsymmetrical pinacols.

It is possible to calculate the course of the rearrangement of a pinacol containing the groups R₂ and R₃ from the results obtained by rearrangement of the pinacols containing a mutual third group R₁ with R₂ and R₁ with R₃. Bachmann and Moser⁴ have found that in symmetrical pinacols such predictions agree closely with the experimental results. In Table II is given a comparison of the calculated and the experimental results obtained with three unsymmetrical pinacols.

Although the calculated figures are of the same order as the experimentally determined values, they do not agree closely and it appears that more than one factor is involved in the rearrangement of an unsymmetrical pinacol.

TABLE II

CALCULATED MIGRATION OF GROUPS
In each case the mutual group R₁ was the phenyl group

Groups R ₂ R ₃	Calcd. Migration	Found
<i>p</i> -Biphenyl : <i>m</i> -tolyl	54:46	58:42
Anisyl : <i>p</i> -tolyl	29:71	45:55
Anisyl : <i>m</i> -tolyl	28:72	35:65

Experimental

Preparation of the Pinacols.—The seven new pinacols were synthesized by the action of a Grignard reagent on the methyl ester of benzoic acid or a substituted benzoic acid. To the solution of Grignard reagent from 0.25 gram mole of aryl halide in 100 cc. of ether was added 100 cc. of benzene and then 0.062 gram mole of ester in portions. After being refluxed the mixture was cooled and hydrolyzed. The crude products were usually digested with cold alcohol or a mixture of alcohol and acetone in order to remove oily impurities before recrystallization. In all cases the pinacols were obtained as colorless crystals. Most of the pinacols hold solvent of crystallization tenaciously; the melting points were determined on samples that had been dried at 60° under reduced pressure. The essential data are presented in Table III.

Preparation of Anisilic Acid.—This acid was prepared by a modification of the Schönberg and Keller⁵ method. Forty grams of anisyl was added to a cooled solution of 24 g. of potassium hydroxide in 150 cc. of absolute alcohol in a 500-cc. bottle; absolute ether was added to fill the bottle. The mixture was shaken for two weeks, one week being found insufficient for complete reaction; yield, 35.8 g. (90%); m. p. 159–160°.

Methyl Anisilate, (CH₃OC₆H₄)₂C(OH)COOCH₃.—The ester was produced in 85% yield by treatment of the acid with a solution of diazomethane. The methyl anisilate was obtained as colorless crystals by recrystallization from a mixture of benzene and petroleum ether; m. p. 110.0–110.5°.

Anal. Calcd. for C₁₇H₁₈O₆: C, 67.5; H, 6.0. Found: C, 67.6; H, 5.9.

Esterification methods which proved unsatisfactory included refluxing the acid with methanol alone or in presence of hydrogen chloride, treatment of the acid with dimethyl sulfate and reaction of the sodium salt with ethyl iodide.

Preparation of 4,4'-Diphenylbenzoic Acid, (C₆H₅-C₆H₄)₂C(OH)COOH.—This acid has been prepared previously only in small amounts. We have worked out a procedure for preparing the compound which depends on the reaction of carbon dioxide with the disodium derivative⁶ of 4,4'-diphenylbenzophenone. Fifteen grams of 4,4'-diphenylbenzophenone⁷ was suspended in a mixture of 150 cc. of anhydrous ether and 150 cc. of ordinary dry benzene in a 350-cc. bottle of the kind employed on a Parr hydrogenation apparatus. Five grams of sodium ribbon was introduced and the reaction was initiated by pressing portions of the sodium with a glass rod until an intense green color developed; if the reaction was not

(5) Schönberg and Keller, *Ber.*, **56**, 1638 (1923).

(6) Schlenk, Appenrodt, Michael and Thal, *ibid.*, **47**, 473 (1914).

(7) Bachmann, *This Journal*, **55**, 773 (1933).

(4) Bachmann and Moser, *ibid.*, **54**, 1124 (1932).

TABLE III
YIELDS AND PROPERTIES OF PINACOLS
Abbreviations: alc, alcohol; ac, acetone; bz, benzene; ch, chloroform

No.	as -benzopinacol	Reactants		Time, hrs.	Yield, %	Recryst. solv.	Cryst. form	M. p., °C.
		Methyl ester of -acid	Grignard re- agent from					
1	3,3'-Dimethyl-4'',4'''- dimethoxy-	Anisilic	<i>m</i> -Bromotoluene	8	49	Ac + alc	Plates	153.3-154.5
2	4,4'-Dimethyl-4'',4'''- dimethoxy-	Anisilic	<i>p</i> -Bromotoluene	8	69	Ac + alc	Heavy needles	159.5-161.0
3	4,4'-Diethoxy-	Benzilic	<i>p</i> -Bromophenetole	9	73	Ac	Prisms	162.0-163.0
4	4,4'-Diphenyl ^a	Benzilic	Bromobenzene	15	86	Ch	Fine needles	190.5-191.0
5	3,3'-Dimethyl-4'',4'''- diphenyl-	Diphenylbenzilic	<i>m</i> -Bromotoluene	19	69	Ch + alc	Needles	160.0-161.0
6	4,4'-Dichloro-	Benzilic	<i>p</i> -Chlorobromobenzene	24	69	Ac ^b	Broad needles	143.0-144.5
7	4,4'-Difluoro-	Benzilic	<i>p</i> -Fluorobromobenzene	24	67	Ac ^c	Needles	166.5-167.5

No.	ac	alc	Solubility bz	ch	Empirical formula	Analyses, %			
						C	Calcd.	H	Found
1	vs	sls			C ₃₀ H ₃₀ O ₄	79.3		6.7	79.1
2	vs	sls			C ₃₀ H ₃₀ O ₄	79.3		6.7	78.8
3	vs	sls			C ₃₀ H ₃₀ O ₄	79.3		6.7	78.9
4	sls		sls	s(h)	C ₃₈ H ₃₀ O ₂	88.0		5.8	87.1
5	s	sls	vs(h)	vs(h)	C ₄₀ H ₃₄ O ₂	87.9		6.3	87.3
6	sls	sls	s		C ₂₆ H ₂₀ O ₂ Cl ₂		Cl, 16.3		Cl, 16.5
7	s	sls			C ₂₆ H ₂₀ O ₂ F ₂		F, 9.4		F, 9.4

^a Almost all of the pinacol precipitated from the solution when the reaction mixture was hydrolyzed.

^b The pinacol holds acetone of crystallization in the ratio of 3 pinacol:2 acetone; these crystals melt at 95°. The solvent is lost at 60° under reduced pressure and can also be eliminated by dissolving the pinacol in ether and evaporating the ether in a current of air.

^c The pinacol crystallizes from acetone with solvent of crystallization; the solvent is lost when the crystals are exposed to air.

started in this manner several days of shaking were sometimes necessary before the reaction began. About a dozen glass beads was added to the mixture, the bottle was stoppered and then shaken mechanically for four or five days. The deep blue solution of the disodium derivative was then shaken for fifteen minutes while it was subjected to one to two atmospheres pressure of carbon dioxide; in five minutes the solution was pale yellow in color, showing that carbonation was complete. The solution was decanted from the excess of sodium and was treated with alcohol until all suspended particles of sodium were destroyed; about 300 cc. of water was added with stirring and in short time the sodium salt of the diphenylbenzilic acid precipitated. The sodium salt was filtered off and was converted to the free acid by digestion with 5% hydrochloric acid for twenty-four hours; yield, 15 g. (88%). By this method we have prepared about 150 g. of diphenylbenzilic acid.

Methyl Ester of 4,4'-Diphenylbenzilic Acid.—Esterification of the acid by a mixture of methanol and hydrogen chloride was unsuccessful; the product was an oil which did not crystallize. Excellent results were obtained by the use of diazomethane. The ester was obtained in clusters of colorless needles by recrystallization from a mixture of benzene and petroleum ether; yield, 89%; m. p. 130.5-131.5°. Methyl diphenylbenzilate is very soluble in hot benzene, soluble in cold benzene and slightly soluble in petroleum ether.

Anal. Calcd. for C₂₇H₂₂O₃: C, 82.2; H, 5.6. Found: C, 82.2; H, 5.6.

Rearrangement of the Pinacols.—Rearrangement was usually attempted by refluxing the pinacol with a mixture of acetyl chloride, acetic acid and benzene.⁴ In two cases, *as*-4,4'-diphenylbenzopinacol and *as*-3,3'-dimethyl-4'',4'''-diphenylbenzopinacol, after the acetyl chloride treatment the mixture was heated with the more powerful reagent iodine in acetic acid⁸ in order to complete the rearrangement; in the case of *as*-4,4'-dichlorobenzopinacol and *as*-4,4'-difluorobenzopinacol only the iodine and acetic acid treatment was employed.

The mixtures of pinacolones were cleaved into triarylmethanes and acids by alcoholic potassium hydroxide; for the concentrated alkali solutions methanol was used as the solvent. The conditions employed for rearrangement and scission and the yields of triarylmethanes and acids are given in Table IV.

Analyses of Acid Mixtures.—The extent of migration undergone by each group in the pinacol was determined by analysis of the acid mixtures. In the mixtures containing anisic acid or phenetic acid the proportion of these acids was estimated by making a methoxyl or ethoxyl determination. The results of different runs checked each other closely.

The mixtures of benzoic acid and *p*-phenylbenzoic acid and of *m*-toluic acid and *p*-phenylbenzoic acid were separated in virtue of the slight solubility of *p*-phenylbenzoic acid in water (0.02 g./100 cc.). *p*-Chlorobenzoic acid was separated from benzoic acid by digestion of the mixture of acids with cold benzene; the latter dissolves

(8) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 237 (1927).

TABLE IV
 REARRANGEMENT OF PINACOLS

<i>as</i> -benzopinacol	Wt. samples, g.	Rearr. time, days	Alc., cc.	Scission KOH, g.	Time, days	Yield of methanes		Yield of acids	
						g.	%	g.	%
3,3'-Dimethyl-4'',4'''-dimethoxy- ^a	1.00	2	100	25	2	0.70	102	0.305	97
	0.45	3	50	3	2	.35	112	.145	98
4,4'-Dimethyl-4'',4'''-dimethoxy- ^a	1.00	5	100	25 ^b	3	.70	102	.305	96
	2.00	3	100	25	3	1.35	99	.620	97
4,4'-Diethoxy- ^a	0.45	3	50	3	2	0.33	104	.120	89
	2.00	4	50	12	2 ^c	1.44	103	.530	89
4,4'-Diphenyl- ^d	0.53	1	100 ^e	10	3	0.37	104	.150	93
	2.00	1	100	10	3	1.43	104	.560	88
	2.00	1	100	10	3	1.45	105	.580	92
3,3'-Dimethyl-4'',4'''-diphenyl- ^f	1.00	1	100	6	2	0.65	96	.270	91
	2.00	1	100	6	1	1.43	104	.585	93
4,4'-Dichloro- ^g	2.00	0.02	100	25	1	1.44	103	.590	93
	3.00	.02	100	25	1	2.08	102	.880	95
4,4'-Difluoro- ^h	2.00	.3	100	25	1	1.34	97	.605	99
	2.00	.3	100	25	1	1.35	97	.590	96

^a Rearranged by heating with 40 cc. of acetyl chloride, 20 cc. of acetic acid and 80 cc. of benzene. ^b Two days with 6% potassium hydroxide gave 40% cleavage; an additional one and one-half days with 15% alkali gave a total of 75% cleavage; 25% potassium hydroxide gave complete scission in three days. ^c Further heating with 25% potassium hydroxide gave no more acid. ^d Heated with 40 cc. of acetyl chloride and 20 cc. of acetic acid; after one day the excess of acetyl chloride was distilled off, 10 cc. of acetic acid and 0.05 g. of iodine was added and the mixture was refluxed for one-half hour. The acetyl chloride treatment alone gave only 35% rearrangement in one day and 50% in two days. ^e Ten cc. of benzene was added to the mixture in order to dissolve the mixture of pinacolones. ^f Treatment as in (d). ^g Refluxed with 50 cc. of acetic acid and 0.05 g. of iodine. ^h Treatment as in (g). Heating with the standard acetyl chloride mixture for four days effected only 10% rearrangement.

benzoic acid to a much greater extent than it does *p*-chlorobenzoic acid. A 0.565-g. sample of a mixture of the two acids was shaken with 17 cc. of benzene and filtered; the residue of *p*-chlorobenzoic acid after being washed with 3 cc. of benzene weighed 0.245 g. A synthetic mixture of similar proportions when treated in the same manner showed that 0.05 g. of *p*-chlorobenzoic acid was dissolved by the benzene; this correction was applied to the weight of acid isolated. The proportion of *p*-fluorobenzoic acid in admixture with benzoic acid was determined by fusing the mixture with sodium peroxide and making a determination of the fluoride radical.⁹

2,2 - Di - *p* - fluorophenyl - 1,2 - diphenylethanone - 1, (FC₆H₄)₂(C₆H₅)CCOC₆H₅.—This pinacolone was readily isolated in a pure state from the mixture obtained by rearrangement of *as*-4,4'-difluorobenzopinacol. By recrystallization from propanol the compound was obtained as colorless cubes; m. p. 121.5–122.5°.

Anal. Calcd. for C₂₆H₁₈OF₂: F, 9.9. Found: F, 9.7.

4,4'-Difluorotriphenylmethane.—This compound was isolated from the mixture of triarylmethanes produced by cleavage of the pinacolones. It was also obtained by scission of the pure 2,2-di-*p* fluorophenyl-1,2-diphenyl-

ethanone-1 and also by reduction of 4,4'-difluorotriphenylcarbinol which was synthesized by interaction of *p*-fluorophenylmagnesium bromide and methyl benzoate. 4,4'-Difluorotriphenylmethane crystallizes in colorless prisms from propanol; m. p. 55–56°.

Anal. Calcd. for C₁₉H₁₄F₂: F, 13.6. Found: F, 13.6.

Summary

Seven new unsymmetrical aromatic pinacols of the type RR(OH)CC(OH)R'R' have been synthesized.

The pinacols have been rearranged to pinacolones and a comparison of the migration aptitudes of the phenyl, *p*-biphenyl, *p*-chlorophenyl, phenetyl, anisyl, *p*-fluorophenyl, *p*-tolyl and *m*-tolyl groups in unsymmetrical pinacolones has been obtained.

It has been found that there is no simple relationship between the values of the migration aptitudes of groups in symmetrical pinacols and the values which hold in unsymmetrical pinacols.

ANN ARBOR, MICH.

RECEIVED AUGUST 31, 1933

(9) Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

